Enhancing the electro-mechanical properties of polydimethylsiloxane elastomers through blending with poly(dimethylsiloxane-co-methylphenylsiloxane) copolymers Acknowledgments

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Enhancing the electro-mechanical properties of polydimethylsiloxane elastomers through blending with poly(dimethylsiloxane-co-methylphenylsiloxane) copolymers

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Abstract

Dielectric elastomers (DEs) hold great promise as materials for novel, advanced electromechanical applications such as actuators, generators and sensors. [1] Choosing the right polymer for the blending approach is of utmost importance to improve the electro-mechanical properties of DEs. [2] A study in our laboratories shows that sub-percentage additions of various aromatic substances can increase electrical breakdown strength significantly via voltage stabilisation, due to an electron trapping effect. [3-5] In this work, improved electro-mechanical properties of silicone-based dielectric elastomers are achieved by means of adding so-called "voltage-stabilisers" prepared from phenyl-functional copolymers prepared using oxyanionic ring-opening polymerisation of octamethylcyclotetrasiloxane (D4) and either tetramethyltetraphenylcyclotetrasiloxane (T4) or octaphenylcyclotetrasiloxane (O4). The concentration of the voltage stabiliser was varied both by changing the molar ratio between methyl and phenyl groups in the copolymer and also by varying the amount of copolymer mixed into a polydimethylsiloxane (PDMS)-based elastomer. The phenyl-functional copolymers were generally found to disperse homogeneously in the PDMS matrix and this resulted in networks with improved mechanical and electrical properties.

Keywords: electro-mechanical properties, silicone dielectric elastomer, voltage stabiliser, phenyl functionalised copolymer, blend

1. Introduction

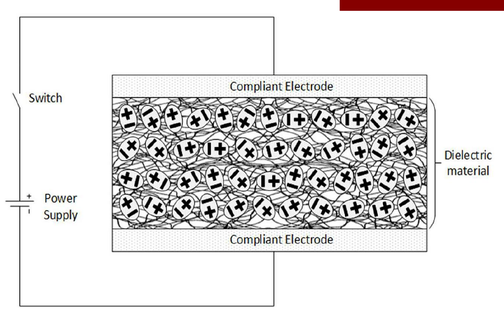


Fig.1 Unpolarised dipoles randomly aligned in the elastomeric matrix.

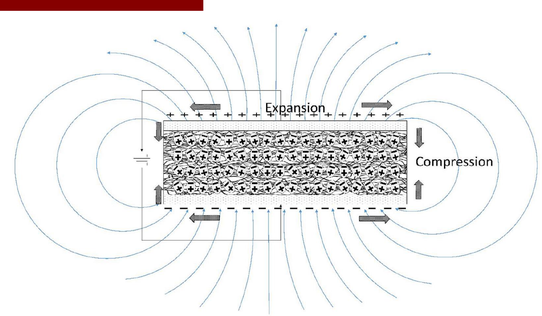


Fig.2 Re-orientation of polarised dipoles in the elastomeric matrix.

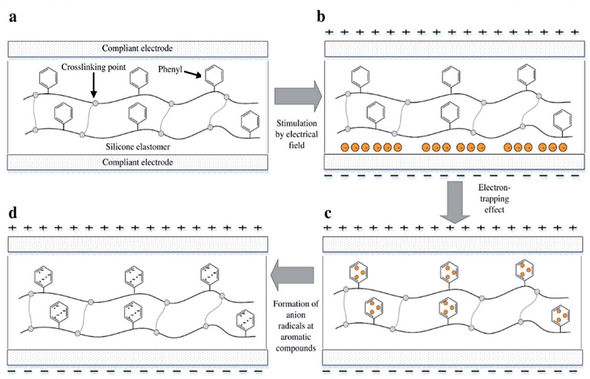


Fig.3 The enhancement of electrical breakdown strength due to electron-trapping: (**a**) a silicone elastomer with an aromatic group grafted to the silicone backbone and a coating of compliant electrodes on the top and bottom surfaces. (**b**) The existence of electrons at the interfaces between the elastomer and the compliant electrode in the presence of an electrical field. (**c**) The electron-trapping effect as a consequence of a collision between electrons and the phenyl group. (**d**) The formation of anion radicals resulting from the disturbance of the cloud of π-electrons of the phenyl group.

2. Experimental

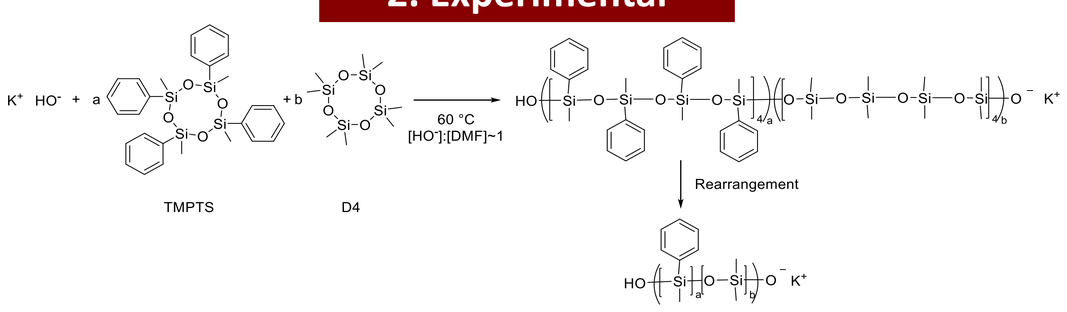


Fig.4 Anionic Ring-Opening Polymerisation of cyclotetrasiloxanes in the presence of N,N-dimethylformamide as a polymerisation promoter.

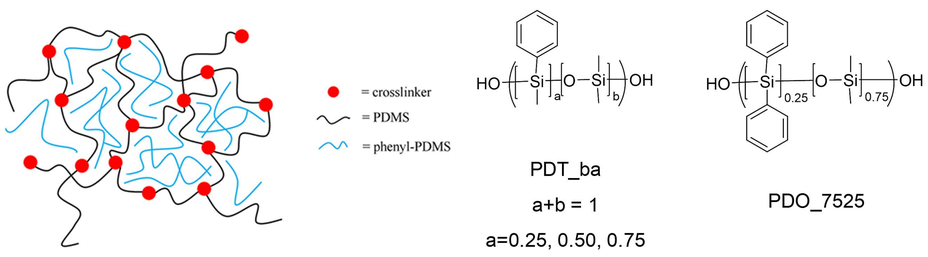
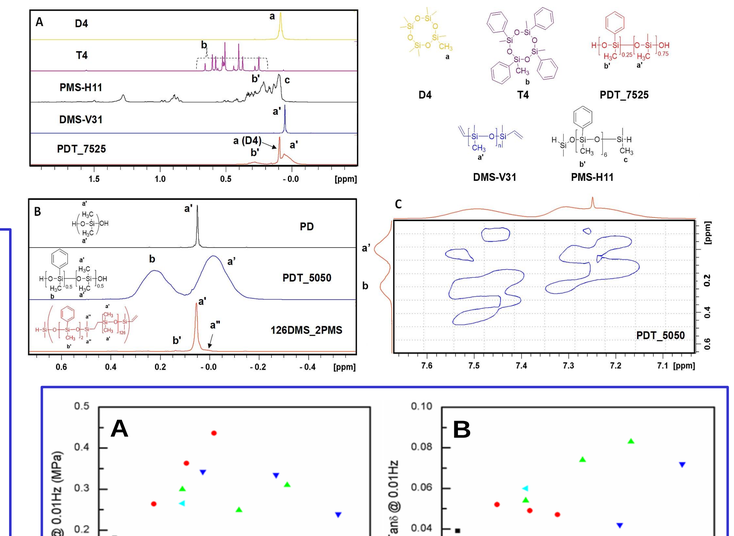


Fig.5 Cross-linked elastomer consisting of phenyl-PDMS copolymer in PDMS matrix and structures of the added phenyl-PDMS copolymers.

3. Results

Fig.6 A) Assigned 1H NMR spectra in the range -0.5 – 1.5 ppm for D4 (yellow), T4 (purple), PMS-H11 (black), DMS-V31 (blue) and PDT_7525 (red). **B**) Partial 1H NMR spectra of PD, PDT_5050 copolymers and the related multiblock copolymer 126DMS_2PMS prepared by step-growth polymerisation as reported earlier.[4] **C**) Partial NOESY spectrum of PDT_5050 showing through-space correlations between aromatic protons and methyl protons.



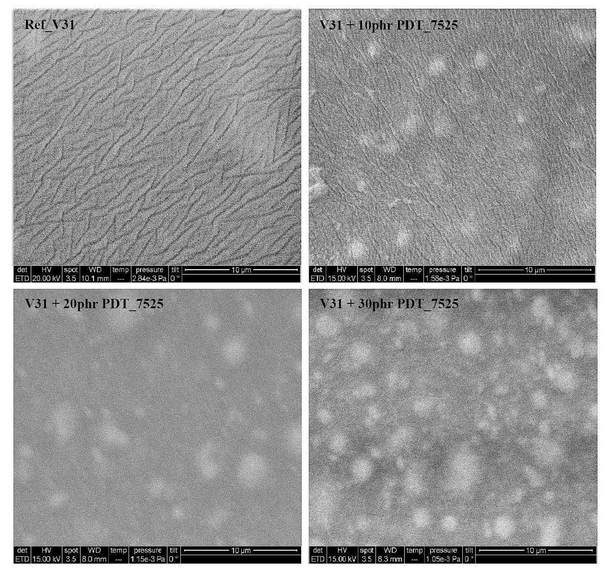


Fig.7 SEM pictures of elastomers with varying loadings of copolymer PDT_7525.

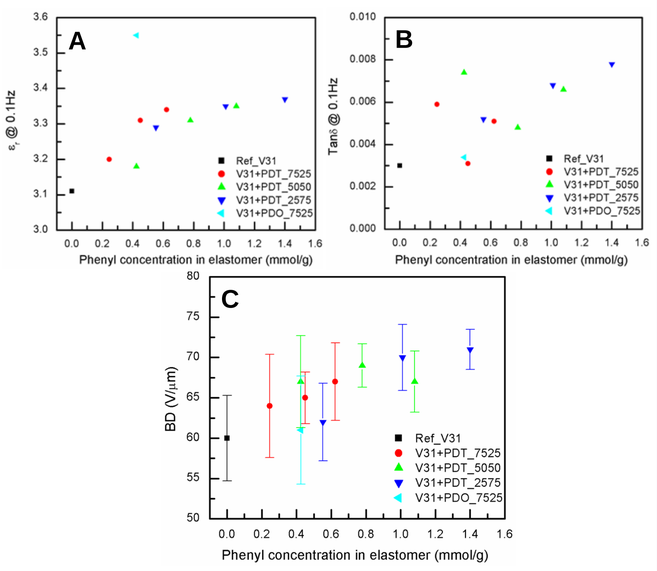


Fig.8 Dielectric properties of elastomers as a function of phenyl concentration for the investigated elastomers at room temperature. **A**) Dielectric permittivity at a frequency of 0.1 Hz. **B**) Dielectric loss at a frequency of 0.1 Hz. **C**) Electrical breakdown strength.

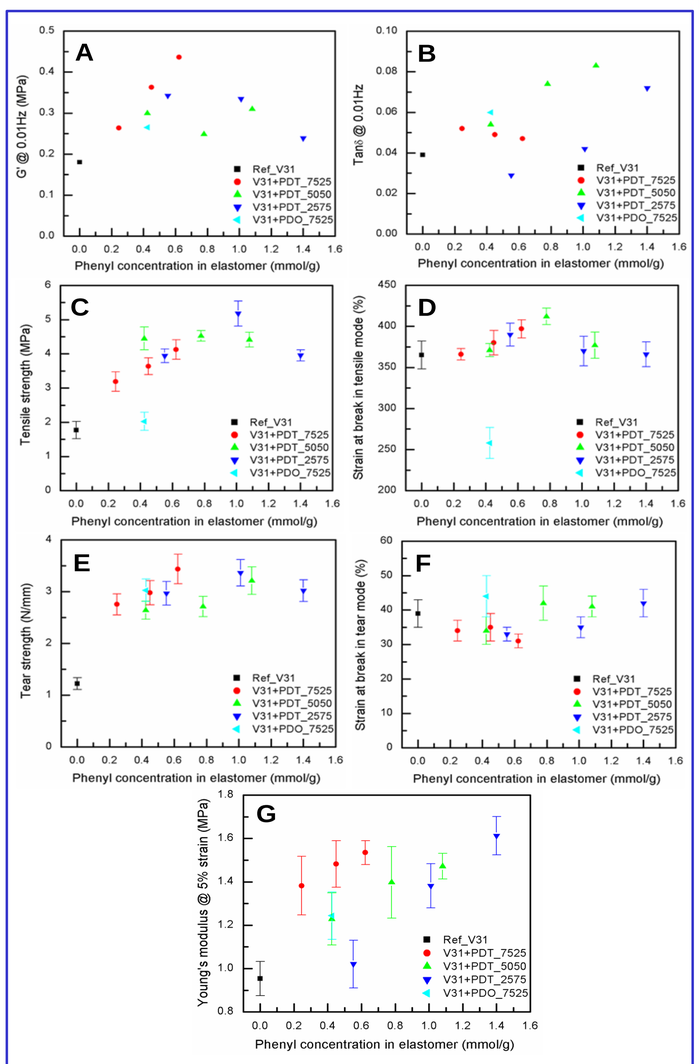


Fig.9 Mechanical properties of elastomers as a function of phenyl content at room temperature. **A**) Storage modulus measured at 2% strain and 0.01 Hz. **B**) Viscous loss measured at 2% strain and 0.01 Hz. **C**) Tensile strength at break. **D**) Strain at break under tensile testing conditions. **E**) Tear strength. **F**) Strain at break under tear testing conditions. **G**) Young's modulus at 5 % strain.

Conclusions

The developed elastomers were inherently extensible with enhanced tensile and tear strengths, due to phenyl-rich microphases acting as reinforcing domains. Furthermore, addition of phenyl-functional copolymers resulted in elastomers with increased relative permittivity and electrical breakdown strength compared to control elastomers while retaining a low dielectric loss. This demonstrates their efficiency as voltage stabilisers.

Table 1 Overall properties of the elastomers.

Sample name	Composition		Theoretical phenyl concentration (mmol g^{-1})	Mechanical properties								Dielectric properties		
	Copolymer	Concentration (phr)		Gel fraction (%)	G' @0.01Hz (MPa)	tanδ @0.01Hz	Y@5%strain (MPa)	Tensile strength (MPa)	Strain at break in tensile mode (%)	Tear strength (N/mm)	Strain at break in tear mode (%)	ε_r @0.1Hz	tanδ @0.1Hz	BD (V/µm)
DMS-V31 (M_n = 28000 g mol^{-1}) (reference)	-	-	0	91.5±0.4	0.18	3.9e-02	1.0±0.1	1.8±0.3	365±17	1.2±0.1	39±4	3.11	3.0e-03	60±5
V31 + 10 phr PDT 7525	PDT_7525 (M_n = 58500 g mol^{-1})	10	0.25	94.4±0.5	0.26	5.2e-02	1.4±0.1	3.2±0.3	366±7	2.8±0.2	34±3	3.20	5.9e-03	64±6
V31 + 20 phr PDT 7525		20	0.45	93.3±0.6	0.36	4.9e-02	1.5±0.1	3.6±0.2	380±15	3.0±0.2	35±4	3.31	3.1e-03	65±3
V31 + 30 phr PDT 7525		30	0.62	91.8±0.3	0.44	4.7e-02	1.5±0.1	4.1±0.3	397±11	3.4±0.3	31±2	3.34	5.1e-03	67±5
V31 + 10 phr PDT 5050	PDT_5050 (M_n = 34500 g mol^{-1})	10	0.42	94.6±0.3	0.30	5.4e-02	1.2±0.1	4.4±0.3	371±8	2.6±0.2	34±4	3.18	7.4e-03	67±6
V31 + 20 phr PDT 5050		20	0.78	92.8±0.2	0.25	7.4e-02	1.4±0.2	4.5±0.2	412±10	2.7±0.2	42±5	3.31	4.8e-03	69±3
V31 + 30 phr PDT 5050		30	1.08	92.0±0.4	0.31	8.3e-02	1.5±0.1	4.4±0.2	377±16	3.2±0.3	41±3	3.35	6.6e-03	67±4
V31 + 5 phr PDT 2575	PDT_2575 (M_n = 31900 g mol^{-1})	5	0.55	94.5±0.3	0.34	2.9e-02	1.0±0.1	3.9±0.2	390±14	3.0±0.2	33±2	3.29	5.2e-03	62±5
V31 + 10 phr PDT 2575		10	1.01	93.7±0.4	0.34	4.2e-02	1.4±0.1	5.2±0.4	370±18	3.4±0.3	35±3	3.35	6.8e-03	70±4
V31 + 20 phr PDT 2575		20	1.40	90.6±0.5	0.24	7.2e-02	1.6±0.1	4.0±0.2	366±15	3.0±0.2	42±4	3.37	7.8e-03	71±2
V31 + 10 phr PDO_7525	PDO_7525 (M_n = 34400 g mol^{-1})	10	0.43	95.0±0.7	0.27	6.0e-02	1.2±0.1	2.0±0.3	258±19	3.0±0.2	44±6	3.55	3.4e-03	61±7

Acknowledgments

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References

1. F. B. Madsen, A. E. Daugaard, S. Hvilsted and A. L. Skov, *Macromol. Rapid Commun.*, 2016, **37**, 378.
2. A. L. Skov and L. Yu, *Adv. Eng. Mater.*, DOI: 10.1002/adem.201700762.
3. A. H. A Razak, P. Szabo and A. L. Skov, *RSC Adv.*, 2015, **5**, 53054.
4. A. H. A Razak and A. L. Skov, *RSC Adv.*, 2017, **7**, 468.
5. A. H. A Razak, L. Yu and A. L. Skov, *RSC Adv.*, 2017, **7**, 17848.